

**Ion Exchange Properties of  
Selected North American Low Rank Coals.**

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**Introduction**

One of the main problems with the use of low rank coal for combustion purposes lies in its inherently high oxygen content. The high oxygen content results in increased coal reactivity and degradation during mining and storage as well as serving to decrease the overall calorific value of the coal. The high oxygen contents of selected low rank coals can, however, be of great value in certain situations, especially with respect to functional groups containing an exchangeable hydrogen ion.

The ability of low rank coals to form stable complexes with several heavy metal ions has long been recognized <sup>(1-8)</sup>. This property has been successfully utilized to estimate the concentration of acidic oxygen functional groups present in low rank coals<sup>(6)</sup> as well as serving as a convenient means of dispersing metal catalysts across a coal surface prior to liquefaction <sup>(9)</sup>. The relatively high ion exchange capacity of several low rank coals studied, coupled with the low overall cost of the bulk material, indicates great potential for the utilization of low rank coals as a means to remove a range of metals from aqueous waste streams.

## Experimental

The lignites chosen for investigation were from A. The Beulah Zap deposit, in Mercer County, North Dakota. B. The Claiborne Deposit in Carlisle County, Western Kentucky and C. The Jackson Group in Atascosa County, Eastern Texas. A sample of brown coal from the Loy Yang coal field in the Latrobe Valley, Victoria, Australia was also included for comparative purposes as its ion exchange properties have been well documented<sup>(1-3)</sup>.

The samples were obtained with a particle size of < 50 mesh and as such no further size reduction was carried out. The samples were received as mined and stored inside double plastic bags to prevent moisture loss from the samples.

Samples of each coal were also petrographically characterized using combined white light and blue light microscopic analysis. Maceral nomenclature was based on descriptions published in Ref.12.

The ion exchange properties of each coal was characterized using batch metal adsorption tests. Metal solutions were made from AR grade reagents and stored in glass volumetric flasks prior to use. No pH adjustment was made to any of the solutions as that would entail the addition of extra competing cations to the solutions and thus interfere with the ion exchange process. Batch ion exchange experiments were performed by shaking 50.0 mL of the metal solution with a pre-weighed mass (equivalent to 2.50 g dry weight) of as-received coal in 125 mL polyethylene bottles. The bottles were shaken for 12 hours on an orbital shaking platform to ensure equilibrium conditions were reached. The samples were allowed to settle for a further 12 hours before the supernatant solution was sampled for metal analysis using Inductively Coupled Plasma Spectrometry.

FTIR spectra were obtained from 0.4% loaded KBr discs using a Nicolet 20SX spectrophotometer. The discs were dried in vacuo over  $P_2O_5$  to minimize interference due to adsorbed  $H_2O$ .

## Results and Discussion

### Petrographical Analysis

The four Tertiary lignites were analyzed petrographically according to humic maceral nomenclature outlined in Stach et al.<sup>(10)</sup> and through ICCP communications. Previous studies of the petrology of the Kentucky and Texas lignites were done by Hower et al.<sup>(11)</sup> and Mukhopadhyay<sup>(12)</sup>.

Mean reflectance was done on uniform ulminite fragments. No polarizer or stage rotation were employed in the reflectance analysis. The Paleocene Beulah-Zap, Mercer County, North Dakota, lignite has the highest reflectance, 0.33%  $R_{mean}$ , followed by the Eocene Jackson Group lignite from Atascosa County, Texas, at 0.28%  $R_{mean}$ . The Eocene Claiborne Formation lignite from Carlisle County, Kentucky, and the Loy Yang lignite from Victoria, Australia, have mean reflectances of about 0.20%. Lower ulminite amounts in

the latter two lignites hindered the reflectance analyses.

The lignites have distinctive maceral compositions. The North Dakota lignite has the highest percentage of relatively "intact" wood-derived macerals: textinite, ulminite, corpohuminite, fusinite, semifusinite versus humodetrinite. The high inertinite concentration of that sample sets it apart from the other samples.

The Texas lignite has over 50% ulminite in contrast to the high humodetrinite concentration in the Kentucky lignite. The Loy Yang lignite has the highest concentration of liptinite macerals with much of the group being liptodetrinite. The Loy Yang lignite appears to have a relatively high concentration of root-derived macerals, particularly suberinite-enclosed rootlets. The contrast between the raw and sized Kentucky and Texas lignites is also distinctive. In both cases much of the relative order of humic maceral percentages is preserved but there is an increase in the percentage of liptinite macerals in the sized fraction. Liptinite contributes to the strength of the particles and tends to be concentrated in the coarser particles. The fine particles would have had a higher percentage of humic macerals, particularly the easily fragmented humodetrinite which was lost in greater proportions than ulminite.

#### **Batch Metal Adsorption Tests.**

Table 2 lists the equilibrium metal concentrations and solution pH's measured after samples of the various lignites were contacted with 1000 ppm solutions of mercury, lead and cadmium at a solid : liquid ratio of 5:100 (measured on a dry coal basis). As expected, equilibrium solution pH was found to be the major factor determining the extent of metal adsorption. Coals that generated the higher solution pH's were found to exhibit the largest metal adsorption capacities. When analyzing solutions that had been treated with either the North Dakota or East Texas lignites, high levels of sodium were detected in the plasma during metal analysis indicating that a large proportion of the carboxylic groups in these coals are naturally present as sodium carboxylates, which explains the relatively high pH's generated in solution. Sodium carboxylates are known to exchange for a divalent cation more readily than protonated groups which accounts for the high level of metal adsorption measured for these lignites. The sample of West Kentucky lignite also displayed a relatively large adsorptive capacity for the metals investigated but did not contain appreciable amounts of sodium (as detected visually in the plasma), although the relatively high pH's generated in solution would indicate that the coal is naturally pre-exchanged with another readily exchangeable cation.

All of the North American lignites investigated showed relatively high adsorptive capacities for each of the metals investigated. Using multi-stage treatments of heavy metal solutions with these lignites, it should therefore be possible to meet EPA discharge limits much more cheaply than using conventional heavy metal treatment processes.

### **Infra Red Spectroscopy**

The FTIR spectra of the ROM (Run Of Mine) coals is presented in Figure 1. The spectra reveal that Loy Yang has the highest concentration of carbonyl/free carboxyl groups followed by Kentucky whilst the Texas and Nth Dakota coals contain relatively few. The spectrum of the Kentucky coal is dominated by strong adsorptions associated with clays/silicates. The Texas lignite, in addition, features adsorptions commonly associated with carbonates. Loy Yang in accord with its low ash yield contains very little adsorption associated with mineral matter.

Acid washing the ROM Kentucky coal converts the carboxylate salts to their corresponding protonated acids, Figure 2. The broad adsorption associated with carboxylates at  $\sim 1575\text{cm}^{-1}$  is merged with the  $\sim 1600\text{cm}^{-1}$  band in the ROM and metal exchanged spectra. Protonation shifts the carbonyl/carboxyl adsorption band back into the  $\sim 1700\text{cm}^{-1}$  region. Figure 2 reveals that the ROM and metal exchanged spectra are equivalent indicating that the ROM coal is naturally present in its fully exchanged form.

The positive bands in the difference spectrum (Loy Yang-Kentucky) in Figure 3, confirm the greater concentration of free carboxyl groups in the Victorian coal.

### **Conclusions**

Three North American lignites were studied in order to characterize their ion exchange properties. All three coals were shown to be capable of adsorbing significant quantities of mercury, cadmium and lead from solution. Infra Red spectroscopy confirmed that the metals were ion exchanged with carboxylic acid functional groups to form metal carboxylates on the coal surface. From these results it would appear that low rank coals show great promise as a means of cheaply removing heavy metal contaminants from aqueous streams. Further studies will concentrate on the ion exchange capacity and selectivity of these coals as well as investigating the possible uses of the ion exchanged coals.

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**Table 1. Petrographic Composition of Lignite Samples.**

	Texas <sup>1</sup>	Texas <sup>2</sup>	Kentucky <sup>1</sup>	Kentucky <sup>2</sup>	N. Dakota	Loy Yang
Textinite	4.5	8.8	4.2	3.8	7.8	11.2
Ulminite	56.9	53.2	18.6	17.0	47.6	14.4
Humodet.	26.1	11.2	50.6	31.8	6.6	22.0
Gelinite			2.0	1.8	0.2	
Corpohum.	3.2	6.6	4.8	7.0	1.4	12.8
Fusinite		0.6	2.2	1.2	19.2	t
Semifusinite	0.6	0.4	1.0	0.2	10.8	
Sclerotinite	0.1	0.2	1.0	1.2		t
Inertodet.					1.2	
Exinite	3.8	4.2	4.6	7.8	2.6	3.2
Resinite	4.6	5.8	2.0	6.8	0.2	10.8
Suberinite	0.1	1.0	0.4	0.2	0.2	3.2
Liptodet.	0.1	7.8	6.4	20.4	2.2	22.4
Alginite			1.2			
R <sub>mean</sub>	0.28		0.20		0.33	0.19

<sup>1</sup> raw sample

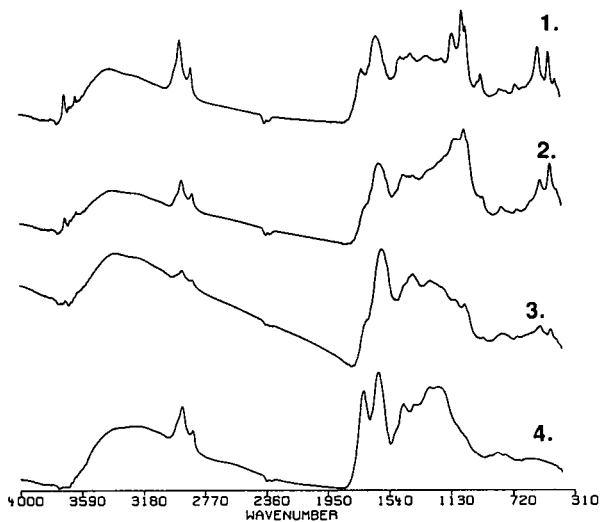
<sup>2</sup> sized sample

**Table 2. Ion Exchange Properties of Selected Lignites.**

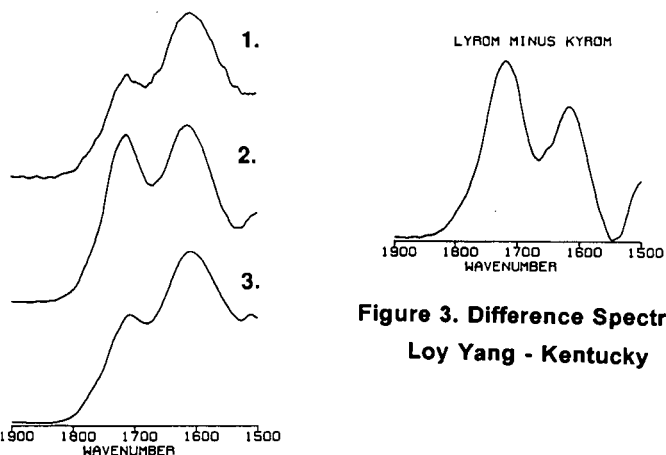
<u>Coal</u>	<u>Mass (wet)</u>	<u>Mass(dry)</u>	<u>Metal</u>	<u>[Metal] (ppm)</u>	<u>pH</u>
Blank			Hg	1175	4.97
Loy Yang	6.82	2.32	(Chloride)	566	3.27
North Dakota	3.28	2.62		12	6.53
Blank			Cd	1105	7.11
Loy Yang	6.82	2.32	(Acetate)	128	4.37
North Dakota	3.15	2.52		45	6.55
Blank				1040	
West Ky.	3.49	2.51		116	4.91
East Tx.	3.35	2.48		78	5.64
Blank			Pb	1069	5.98
Loy Yang	6.70	2.28	(Acetate)	30	3.98
North Dakota	2.93	2.34		5	6.72
Blank				1005	
West Ky.	3.47	2.50		7	4.83
East Tx.	3.34	2.47		2	5.74

Coal shaken with 50.0 mL of solution for 12 hours, allowed to settle for approx. 5 hrs and the supernatant sampled for residual metal analysis.

Moistures:	Loy Yang	(Latrobe Valley, Victoria, Australia)	66%
	North Dakota	(Beulah Zap, Mercer Co. ND)	20%
	East Texas	(Jackson Fm, Atascosa Co. Tx)	26%
	West Kentucky	(Claiborne Fm., Carlisle Co., Ky)	28%



**Figure 1. Infra Red Spectra of As-Received Coals**  
 1. Kentucky 2. Texas 3. North Dakota 4. Loy Yang



**Figure 3. Difference Spectra:**  
 Loy Yang - Kentucky

**Figure 2. Infra Red Spectra of Kentucky Lignite**  
 1. As-Received 2. Acid Extracted 3. Metal Exchanged.